Application No.: 10/583,762 Docket No. : 2006_0963A

EXHIBIT

(21 pages total, including cover)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of : Naohiro SONOBE et al. Application S.N.: 10/583,762 Filed: June 21, 2006	Attorney Docket No.2006_0963A **Confirmation No.8704** Group Art Unit: 1793 Examiner: Guinever S. Gregorio
MATERIAL FOR NEGATIVE ELECTRODE OF NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY, PROCESS FOR PRODUCING THE SAME, NEGATIVE ELECTRODE AND BATTERY	**Mail Stop : AF**

DECLARATION UNDER 37 CFR 1.132

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

I, the undersigned, Naohiro SONOBE, hereby declare as follows:

1. I am a citizen of Japan and a resident of 16, Ochiai, Nishikimachi, Iwaki-shi, Fukushima-ken, Japan.

2. In March 1990, I received my Doctor of Engineering degree in Applied Chemistry from the Faculty of Engineering at graduate school of the Tohoku University based on a doctoral thesis entitled "Study on Synthesis of Two-Dimensional Carbon by Using Layered Clay Mineral". Since April 1990, I have been employed at Kureha Corporation (formerly, Kureha Chemical Industry Company, Limited) and have conducted research and development in the field of, among others, production and application of various forms of carbon materials at Research Center of Kureha Corporation. At present, I work as a General Manager of Advanced Material Laboratory in Research Center of Kureha Corporation.

3. I am an author of papers, among others, Naohiro SONOBE, Takashi KYOTANI, Yoshihiro HISHIYAMA, Minoru SHIRAISHI and Akira TOMITA:

"Formation of Highly Oriented Graphite from Poly(acrylonitrile) Prepared Between the Lamellae of Montmorillonite ", *J. Phys. Chem.,* 92 (24), pp. 7029 - 7034; and Naohiro SONOBE, Takashi KYOTANI and Akira TOMITA: "Carbonization of Polyacrylonitrile in a Two-Dimensional Space Between Montmorillonite Lamellae", ***Carbon***, **26**, pp. 573 – 578 (1988). I am an inventor of, among others, U.S. Patents Nos. 7,781,370, 7,651,974, 7,651,817, and 7,634,840, directed to production and application of various forms of carbon materials. I am now an accredited member of The carbon Society of Japan

4. I am one of the applicants of the application S.N.: 10/583,762 (hereinafter referred to as the instant application) and accordingly I am familiar with the specification and claims of the instant application.

5. Moreover, I have read carefully and I am familiar with the Official Action dated April 15, 2010, which action rejected Claims 1 – 4 and 6 – 13 of the instant application. I have read carefully and I am familiar with several references, inclusive of Kwon et al. (WIPO Pub. No.02/083557A1, hereinafter simply referred to as "Kwon"), Sonobe et al. (U.S. Pat. No. 5,857,525), Sonobe et al. (U.S. Pat. No. 5,616,437), Nagamine et al. (U.S. Pat. No. 5,932,373), Yoon et al. (U.S. Pat. No. 6,281,050 B1), Sonobe et al. (U.S. Pat. No. 5,527,643), and Lu et al. (Anodic Performance of Vapor-Derived Carbon Filaments in Lithium-Ion Secondary Battery; Carbon, 39,493 – 496 (2001)) cited for rejecting the above-mentioned claims.

I have also read and familiar with the Advisory Action dated July 28, 2010, which action confirmed the rejection of Claims 1 – 3 and 6 – 13 of the instant application.

The substance of the Examiner's rejection is believed to be based on the conclusion that Claims 1 – 3 and 6 – 13 are unpatentable over Kwon in view of the secondary references and, particularly that Kwon discloses spherical carbon particles substantially satisfying the morphological limitations recited in Claim 1 of the instant application. In the Advisory Action, the Examiner criticized the calculation of a particle size disperse factor D_4/D_1 of the Kwon's particles submitted in the Applicant's response dated July 15, 2010.

6. In order to try to traverse the Examiner's conclusion, I have decided to submit this Declaration comprising (1) re-submission of the calculation of a particle size disperse factor D_4/D_1 of the Kwon's particles while noting the Examiner's criticism expressed in the Advisory Action and (2) a report of Experiment for substantially reproducing Example 1 of the instant application,

which Experiment was conducted, under my direction and control, for re-procuring spherical carbon particles of the instant application to provide a SEM (scanning electron microscope) picture showing morphological characteristics of the spherical carbon particles compared with those of Kwon

[Part 1: Re-submission of the calculation of a particle size dispersion factor D_4/D_1 of the Kwon's particles]

A particle size disperse factor D_4/D_1 was calculated as described in [0019] of the instant application, based on the graph in Fig. 4 of Kwon. First, an enlarged copy of Fig. 4 was obtained by utilizing an enlarging function of an electrophotographic copier, and a vertical length was measured by a scale at each particle size (D) on an abscissa of the enlarged copy as it represents (i.e., is proportional to) a volume (i.e., weight)-basis frequency (nD^3). The vertical scale of Fig. 4 of Kwon is assumed to represent a volume-basis frequency (nD^3). This assumption is based on the following reason. I attach hereto copies of the following two references:

Ref. 1: M.W. Wedd: "Determination of Particle Size Distributions Using Laser Diffraction",
(an ouput from Internet address< http://erpt.org/032Q/Wedd-00.htm>) ,and
Ref. 2: an output from Internet address <http://chemeurope.com.artcles/ e/61205/ >

These references both show that Using Laser Diffraction is a dominant method of choice for determining particle size distributions ,and the output from laser beam diffraction instruments is usually reported as a volume-basis distribution (rather than a number-basis distribution) for respective sizes. This is discussed in the paragraph bridging pages 2 and 3 of Ref. 1 and corroborated by Figs. 4 and 6 of Ref. 2.

In view of such a trend and the wide particle size range (of 0.01 μm to 100 μm) which is shown in Fig. 4 of Kwon and also a characteristic of the laser diffraction method, it is believed reasonable to assume that the particle size distribution shown in Fig. 4 is on a volume-basis, unless there is found a special remark contrary to the usual expression.

Moreover, the number-basis frequency (nD) of Kwon's product provides a peak of frequency at a much smaller particle size than 16 μm as now shown in Fig. 4 in view of abundance in number of 3 – 4 μm particles shown in Fig. 3 (a SEM picture) corresponding to the graph of Fig. 4.

The measured vertical lengths based on the above assumption, and calculated data of nD^3, nD, n and nD^4 based thereon, are inclusively shown in Table A attached hereto. Incidentally, from the thus-obtained data of volume-basis frequency nD^3 at corresponding size D, nD, n and nD^4 required for calculating D_4/D_1 are calculated as follows: $nD = nD^3/ D^2$, $n = nD^3 /D^3$ and $nD^4 = nD^3 \times D$.

Table A also shows calculated ΣnD^3, ΣnD , Σn and ΣnD^4 , and also $D_1 =$

$\Sigma nD/\Sigma n$, $D_4 = \Sigma nD^4/\Sigma nD^3$ and D_4/D_1, calculated based thereon. These calculations were performed by using a table-calculation software "Excel" available from Microsoft Co., and Table A is a print-out of an output of Excel data.

At the end, Table A shows a calculated particle size disperse factor D_4/D_1 of 7.05, which is much larger than the upper limit of 3.0 recited in Claim 1 of the instant application.

Incidentally, Fig. 4 of Kwon lacks a frequency data at a particle size of 1.625 μm, and it is regarded as 0 mm in Table A. Table B also attached hereto was obtained by regarding the frequency data at 1.625 μm as 7 mm by interpolation between (substantially identical to) those at 1.5 μm and 1.75 μm on both sides, and Table B thus obtained shows a substantially identical particle size disperse factor D_4/D_1 of 7.04.

[Part 2: EXPERIMENT]

(Experiment 1)

The polymerization process in Example 1 of the instant application was substantially repeated. As a result, true-spherical vinyl resin particles having an average particle size (Dv_{50}) of about 15 μm were obtained.

40 g of the thus-obtained true-spherical vinyl resin particles were spread in a small thickness in a stainless steel vat and subjected to 1 hour of oxidation at 280°C in a muffle furnace to form a spherical carbon precursor. The spherical carbon precursor in an amount of 30 g was charged on a dispersion plate placed in a quartz-made vertical tubular furnace, and nitrogen was blown upwards in the furnace to form a fluidized bed of the carbon precursor, which was then heat-treated for 1 hour to form a preliminarily calcined carbon. The calcined carbon was then placed in a horizontal tubular furnace, heated to 1200°C in a nitrogen atmosphere and retained for 1 hour for main calcination, followed by cooling to form spherical carbon particles having an average particle size of 11 μm.

Some of the thus-obtained spherical carbon particles were observed through a SEM (scanning electron microscope) ("JSM-5510LV", made by JEOL Ltd.) at a magnification of x 1000 at an acceleration voltage of 10 kV and photographed. A print-out copy of the resultant photograph is attached hereto as Photo C (at a print-out magnification of about 2000). Photo C shows that the resultant carbon particles are much more spherical than those shown in Figs. 1 – 3 and 7 of Kwon

About 0.1g of the remaining spherical carbon particles was subjected to measurement of particle size distribution in a particle size range of 0.5 – 3000 μm by using a particle size distribution meter ("SALD-3000S", made by Shimadzu Corporation), similarly as described in paragraph [0047] of the instant application. An output sheet of the particle size distribution meter is attached hereto as Sheet D together with Sheet Da including some English denotations.

From the particle size distribution data shown on Sheet D, data for calculating a particle size disperse factor as shown in Table A were gathered to provide Table E similarly as was done for Table A. Differential frequency value "q3(%)" on Sheet D corresponds to "nD3" in Table E. The thus-obtained Table E shows a particle size disperse factor D_4/D_1 of 1.24 which is much smaller than 7.05 for Kwon shown in Table A.

<<Evaluation>>

The above experimental results as well as the data shown in Table 1 of the instant application are believed to show that the spherical carbon particles obtained by the instant invention are much more spherical than and have a remarkably narrower particle size distribution compared with the carbon particles of Kwon

Such a broad particle size distribution and a lower sphericity of carbon particles of Kwon are understandable from its production process.

Kwon's process (e.g., as recited in claim 7 or 8) includes step a) of heat-treating a mixture of a carbon precursor (such as a resin or pitch) and a dispersion media (hydrophobic inorganic substance or silicone oil) at a glass transition temperature or softening temperature of the carbon precursor to 300 ℃ to make the carbon precursor spherical.

The carbon precursor is in a solid powder form that can be mixed with a dispersion media, i.e., a hydrophobic inorganic substance or silicone oil. (page 11, lines 18 – 20).

The hydrophobic inorganic substance or silicone oil is distributed on the surfaces of carbon precursor particles to restrain the cohesion of carbon precursor particles and provides a high surface tension to make the particles convert into spherical form.(page 8, lines 2 – 24). This solid powder-form (volume-basis) distribution is considered to determine the particle size distribution of the product carbon particles since the cohesion of the particles is prevented thereafter.

Kwon adopts pulverization as means for converting the carbon precursor into a solid powder form for pitch in Example 12 and for phenolic resin in Example 14 (pages 12 – 15). As is already admitted by Kwon per se, pulverized solid particles (not only of carbon) have non-spherical irregular shapes (page 7, lines 16 – 21; page 7, lines 19 – 21). The pulverization is also well known to result in a powder having a broad particle size distribution. The adoption of solid pulverization for providing carbon precursor particles in Kwon is thus a reason for providing product carbon particle having an inevitably broad particle size distribution and a lower sphericity.

In contrast thereto, in the instant invention, the carbon precursor particles are spherical vinyl resin particles obtained through suspension polymerization, wherein a vinyl monomer in an easily dispersible and deformable liquid state is subjected to a uniform stirring shearing force into fine spherical droplets having a narrow size distribution and the resultant uniformly dispersed droplets are solidified into the solid vinyl resin particles while retaining their spherical shape and uniform size distribution. This is the reason why the spherical carbon electrode material of the present invention retains a very narrow particle size distribution as represented by a particle size disperse factor D_4/D_1 of at most 3.0 as recited in the independent claims, and 1. 23 – 1.33 in Example 1 – 10 of the instant specification.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Dated: October 25, 2010

Naohiro Sonobe
Naohiro SONOBE

Attachments:

- Table A: Calculation of particle size disperse factor D_4/D_1, based on Fig. 4 of Kwon (WO 02/083557A)

- Table B: Calculation of particle size disperse factor D_4/D_1, based on Fig. 4 of Kwon (WO 02/083557A) for the Examiner's consideration

- Photo C: A SEM photograph (at a print-out magnification of about 2000) of spherical carbon particles produced in Experiment 1

- Sheet D: An output sheet from a particle size distribution meter showing particle size dispersion of spherical carbon particles produced in Experiment 1
- Sheet Da: Sheet D modified to include some English denotations

- Table E: Calculation of particle size disperse factor D_4/D_1, based on Sheet D

- Print-out copy of Ref. 1: M.W. Wedd: "Determination of Particle Size Distributions Using Laser Diffraction",
  (an ouput from Internet address< http://erpt.org/032Q/Wedd-00.htm>) ,and

- Print-out copy of Ref. 2: an output from Internet address <http://chemeurope.com.artcles/>

Table A: Calculation of particle size disperse factor D_4/D_1based on Fig. 4 of Kwon (WO 02/083557A)

		Volume-basis distribution (frequency)				
No	Size: D (μm)	Relative length measured by a scale (mm))	nD^3 (%)	nD	n	nD^4
1	0.8	3	0.18121	0.283147	0.353933857	0.144971
2	0.9	4	0.24162	0.298295	0.331438747	0.217457
3	1	4.5	0.27182	0.271821	0.271821202	0.271821
4	1.125	5	0.30202	0.238636	0.212120798	0.339777
5	1.25	6.5	0.39263	0.251284	0.20102688	0.490788
6	1.375	7	0.42283	0.223647	0.162652507	0.581395
7	1.5	7	0.42283	0.187926	0.125283846	0.634249
8	1.625	0	0.00000	0	0	0
9	1.75	7	0.42283	0.138068	0.07889595	0.739958
10	1.8725	8	0.48324	0.137822	0.073602967	0.904863
11	2	8.5	0.51344	0.12836	0.064180006	1.02688
12	2.2	8	0.48324	0.099842	0.045382954	1.063123
13	2.4	9.5	0.57384	0.099626	0.041510761	1.377227
14	2.6	10.5	0.63425	0.093824	0.03608611	1.649049
15	2.8	12	0.72486	0.092456	0.033020068	2.029598
16	3	13.5	0.81546	0.090607	0.030202356	2.446391
17	3.2	15.5	0.93627	0.091433	0.028572785	2.996074
18	3.4	18	1.08728	0.094056	0.027663464	3.696768
19	3.6	20	1.20809	0.093217	0.025893652	4.349139
20	3.8	22	1.32890	0.092029	0.024218247	5.049834
21	4	24.5	1.47992	0.092495	0.023123679	5.919662
22	4.33	27	1.63093	0.086988	0.020089582	7.061915
23	4.66	29	1.75174	0.080667	0.017310558	8.163093
24	5	31.5	1.90275	0.07611	0.015221987	9.513742
25	5.5	35.5	2.14437	0.070888	0.012888759	11.79402
26	6	37	2.23497	0.062083	0.010347103	13.40985
27	6.5	39	2.35578	0.055758	0.008578184	15.31259
28	7	40	2.41619	0.04931	0.007044281	16.91332
29	7.5	41	2.47659	0.044028	0.005870443	18.57445
30	8	42	2.53700	0.039641	0.004955074	20.29598
31	8.5	42	2.53700	0.035114	0.004131077	21.56448
32	9	42	2.53700	0.031321	0.003480107	22.83298
33	9.5	44	2.65781	0.029449	0.003099936	25.24917
34	10	47.5	2.86922	0.028692	0.002869224	28.69224
35	11	58	3.50347	0.028954	0.002632211	38.53821
36	12	68.5	4.13772	0.028734	0.002394515	49.65267
37	13	79.5	4.80217	0.028415	0.002185787	62.42827
38	14	88	5.31561	0.02712	0.001937177	74.4186
39	15	94	5.67804	0.025236	0.001682383	85.17064
40	16	97	5.85926	0.022888	0.001430483	93.74811
41	17	93	5.61764	0.019438	0.001143423	95.49985
42	18	84	5.07400	0.01566	0.000870027	91.33192
43	19	70.5	4.25853	0.011796	0.000620868	80.91211
44	20	59	3.56388	0.00891	0.000445485	71.27756
45	21.66	47.5	2.86922	0.006116	0.000282351	62.14739
46	23.33	39	2.35578	0.004328	0.00018552	54.96043
47	25	31	1.87255	0.002996	0.000119843	46.81365
48	26.66	20	1.20809	0.0017	6.37559E-05	32.20779
49	28.33	10.5	0.63425	0.00079	2.78946E-05	17.96829
50	30	4.5	0.27182	0.000302	1.00675E-05	8.154636
	Total→	1655.5	100	4.022025	2.322548942	1220.537
			↑ ΣnD^3	↑ ΣnD	↑ Σn	↑ ΣnD^4

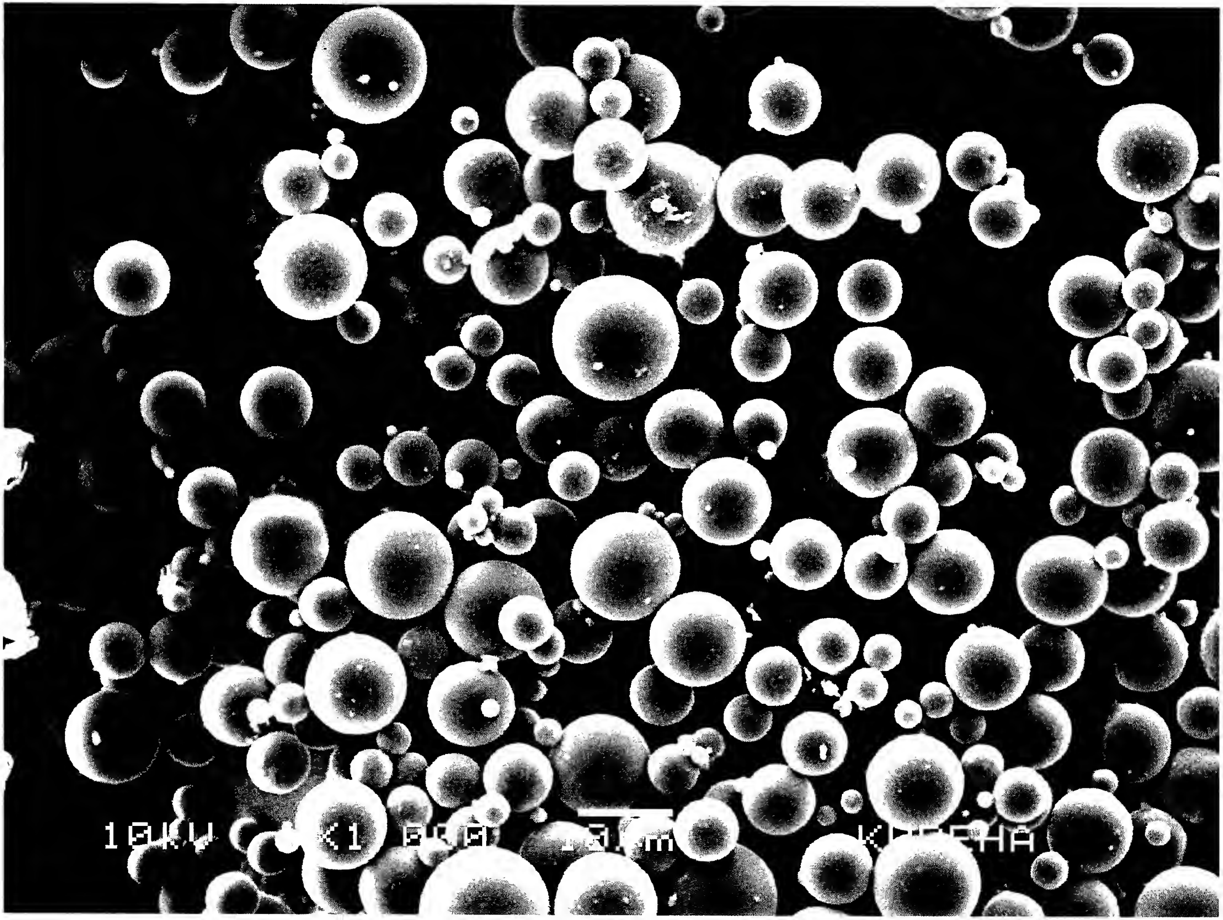
Length-average particle size $D1=\Sigma nD/\Sigma n$	1.73
Volume-average particle size$D4=\Sigma nD^4/\Sigma nD^3$	12.21
Prticle size disperse factor D4/D1	**7.05**

Table B: Calculation of particle size disperse factor D_4/D_1based on Fig. 4 of Kwon (WO 02/083557A)

		Volume-basis distribution (frequency)				
No	Size: D (μm)	Relative length measured by a scale(mm))	nD^3 (%)	nD	n	nD^4
1	0.8	3	0.18045	0.281955	0.352443609	0.144361
2	0.9	4	0.24060	0.297039	0.330043215	0.216541
3	1	4.5	0.27068	0.270677	0.270676692	0.270677
4	1.125	5	0.30075	0.237631	0.211227658	0.338346
5	1.25	6.5	0.39098	0.250226	0.200180451	0.488722
6	1.375	7	0.42105	0.222706	0.161967654	0.578947
7	1.5	7	0.42105	0.187135	0.124756335	0.631579
8	1.625	7	0.42105	0.159452	0.098124236	0.684211
9	1.75	7	0.42105	0.137487	0.078563756	0.736842
10	1.8725	8	0.48120	0.137241	0.07329306	0.901053
11	2	8.5	0.51128	0.12782	0.063909774	1.022556
12	2.2	8	0.48120	0.099422	0.045191868	1.058647
13	2.4	9.5	0.57143	0.099206	0.041335979	1.371429
14	2.6	10.5	0.63158	0.093429	0.035934169	1.642105
15	2.8	12	0.72180	0.092067	0.032881036	2.021053
16	3	13.5	0.81203	0.090226	0.030075188	2.43609
17	3.2	15.5	0.93233	0.091048	0.028452479	2.983459
18	3.4	18	1.08271	0.09366	0.027546987	3.681203
19	3.6	20	1.20301	0.092825	0.025784626	4.330827
20	3.8	22	1.32331	0.091642	0.024116276	5.028571
21	4	24.5	1.47368	0.092105	0.023026316	5.894737
22	4.33	27	1.62406	0.086622	0.020004994	7.03218
23	4.66	29	1.74436	0.080328	0.017237671	8.128722
24	5	31.5	1.89474	0.075789	0.015157895	9.473684
25	5.5	35.5	2.13534	0.07059	0.01283449	11.74436
26	6	37	2.22556	0.061821	0.010303537	13.35338
27	6.5	39	2.34586	0.055523	0.008542065	15.24812
28	7	40	2.40602	0.049102	0.007014621	16.84211
29	7.5	41	2.46617	0.043843	0.005845725	18.49624
30	8	42	2.52632	0.039474	0.004934211	20.21053
31	8.5	42	2.52632	0.034966	0.004113683	21.47368
32	9	42	2.52632	0.031189	0.003465454	22.73684
33	9.5	44	2.64662	0.029325	0.003086883	25.14286
34	10	47.5	2.85714	0.028571	0.002857143	28.57143
35	11	58	3.48872	0.028832	0.002621128	38.37594
36	12	68.5	4.12030	0.028613	0.002384433	49.44361
37	13	79.5	4.78195	0.028296	0.002176584	62.16541
38	14	88	5.29323	0.027006	0.001929021	74.10526
39	15	94	5.65414	0.025129	0.001675299	84.81203
40	16	97	5.83459	0.022791	0.00142446	93.35338
41	17	93	5.59398	0.019356	0.001138609	95.09774
42	18	84	5.05263	0.015595	0.000866363	90.94737
43	19	70.5	4.24060	0.011747	0.000618254	80.57143
44	20	59	3.54887	0.008872	0.000443609	70.97744
45	21.66	47.5	2.85714	0.00609	0.000281162	61.88571
46	23.33	39	2.34586	0.00431	0.000184739	54.72902
47	25	31	1.86466	0.002983	0.000119338	46.61654
48	26.66	20	1.20301	0.001693	6.34875E-05	32.07218
49	28.33	10.5	0.63158	0.000787	2.77772E-05	17.89263
50	30	4.5	0.27068	0.000301	1.00251E-05	8.120301
	Total→	1662.5	100	4.164542	2.410894025	1216.082
			↑ ΣnD^3	↑ ΣnD	↑ Σn	↑ ΣnD^4

Length-average particle size $D1 = \Sigma nD/\Sigma n$	1.73
Volume-average particle size$D4 = \Sigma nD^4/\Sigma nD^3$	12.16
Prticle size disperse factor D4/D1	**7.04**

Photo C:

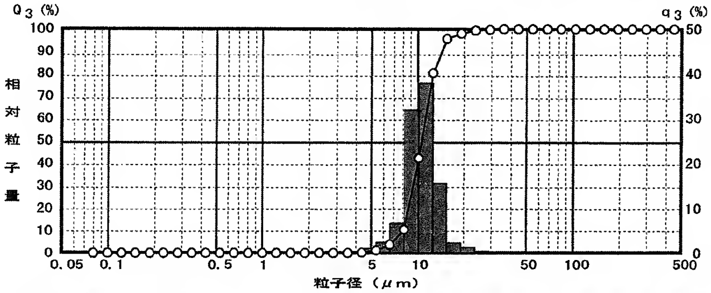

10KV
X1,500
10μm
KUREHA

Sheet D:

島津　SALD-3000S　(SALD-3000-WJA2:V1.01)

（ファイル 名）H100519-06C
（サンプル ID）H100519-06C　　（サンプル #）1
（測定年月日 ）10/05/21　　（ 測定 時間 ）14:40:15

屈折率＝1.70 − 0.20i	ﾒﾃﾞｨｱﾝ径：10.608 モード径：11.295	平均値　：10.555 標準偏差：0.108	10.0%D ：8.114 50.0%D ：10.608 90.0%D ：14.315	Sﾚﾍﾞﾙ　：0 分布関数：無 Dｼﾌﾄ　：0



	粒子径 x(μm)	積算値 Q3(%)	差分値 q3(%)		粒子径 x(μm)	積算値 Q3(%)	差分値 q3(%)		粒子径 x(μm)	積算値 Q3(%)	差分値 q3(%)
1	3000.000	100.000	0.000	18	83.551	100.000	0.000	35	2.327	0.000	0.000
2	2430.192	100.000	0.000	19	67.682	100.000	0.000	36	1.885	0.000	0.000
3	1968.611	100.000	0.000	20	54.826	100.000	0.000	37	1.527	0.000	0.000
4	1594.701	100.000	0.000	21	44.413	100.000	0.000	38	1.237	0.000	0.000
5	1291.810	100.000	0.000	22	35.977	100.000	0.080	39	1.002	0.000	0.000
6	1046.449	100.000	0.000	23	29.144	99.920	0.460	40	0.812	0.000	0.000
7	847.691	100.000	0.000	24	23.608	99.460	1.330	41	0.658	0.000	0.000
8	686.684	100.000	0.000	25	19.124	98.130	2.250	42	0.533	0.000	0.000
9	556.258	100.000	0.000	26	15.492	95.870	15.660	43	0.431	0.000	0.000
10	450.605	100.000	0.000	27	12.549	80.220	37.870	44	0.350	0.000	0.000
11	365.019	100.000	0.000	28	10.166	42.340	31.870	45	0.283	0.000	0.000
12	295.688	100.000	0.000	29	8.235	10.470	6.710	46	0.229	0.000	0.000
13	239.527	100.000	0.000	30	6.671	3.760	2.410	47	0.186	0.000	0.000
14	194.032	100.000	0.000	31	5.404	1.350	1.060	48	0.150	0.000	0.000
15	157.178	100.000	0.000	32	4.377	0.290	0.270	49	0.122	0.000	0.000
16	127.324	100.000	0.000	33	3.546	0.020	0.020	50	0.099	0.000	0.000
17	103.141	100.000	0.000	34	2.873	0.000	0.000	51	0.080	0.000	0.000

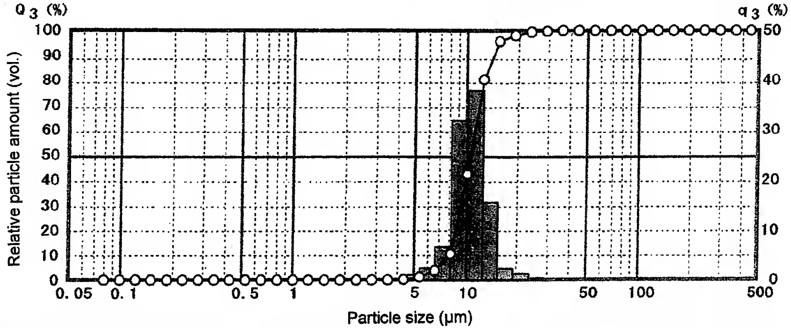
サンプリング：マニュアル　　屈 折 率　：1.70-0.20i
測定回数：　1　測定間隔(秒)：___　　平均回数　：　64
測定吸光度範囲（最大値）：0.200　（最小値）　：0.010
超音波照射時間(秒)：___　　分散時間(秒)：___

Sheet Da:

島津　SALD-3000S　(SALD-3000-WJA2:V1.01)

（ファイル 名）H100519-06C
（サンプル ID）H100519-06C　　（サンプル #）1
（測定年月日 ）10/05/21　　（ 測定 時間 ）14:40:15

屈折率＝1.70 － 0.20i	ﾒﾃﾞｨｱﾝ径:　10.608 モード径:　11.295	平均値　:　10.555 標準偏差:　0.108	10.0%D :　8.114 50.0%D :　10.608 90.0%D :　14.315	Sﾚﾍﾞﾙ　: 0 分布関数:無 Dｼﾌﾄ　: 0



	particle size x (μm)	cumulative value Q3 (%)	differential value q3 (%)		particle size x (μm)	cumulative value Q3 (%)	differential value q3 (%)		particle size x (μm)	cumulative value Q3 (%)	differential value q3 (%)
1	3000.000	100.000	0.000	18	83.551	100.000	0.000	35	2.327	0.000	0.000
2	2430.192	100.000	0.000	19	67.682	100.000	0.000	36	1.885	0.000	0.000
3	1968.611	100.000	0.000	20	54.826	100.000	0.000	37	1.527	0.000	0.000
4	1594.701	100.000	0.000	21	44.413	100.000	0.000	38	1.237	0.000	0.000
5	1291.810	100.000	0.000	22	35.977	100.000	0.080	39	1.002	0.000	0.000
6	1046.449	100.000	0.000	23	29.144	99.920	0.460	40	0.812	0.000	0.000
7	847.691	100.000	0.000	24	23.608	99.460	1.330	41	0.658	0.000	0.000
8	686.684	100.000	0.000	25	19.124	98.130	2.250	42	0.533	0.000	0.000
9	556.258	100.000	0.000	26	15.492	95.870	15.660	43	0.431	0.000	0.000
10	450.605	100.000	0.000	27	12.549	80.220	37.870	44	0.350	0.000	0.000
11	365.019	100.000	0.000	28	10.166	42.340	31.870	45	0.283	0.000	0.000
12	295.688	100.000	0.000	29	8.235	10.470	6.710	46	0.229	0.000	0.000
13	239.527	100.000	0.000	30	6.671	3.760	2.410	47	0.186	0.000	0.000
14	194.032	100.000	0.000	31	5.404	1.350	1.060	48	0.150	0.000	0.000
15	157.178	100.000	0.000	32	4.377	0.290	0.270	49	0.122	0.000	0.000
16	127.324	100.000	0.000	33	3.546	0.020	0.020	50	0.099	0.000	0.000
17	103.141	100.000	0.000	34	2.873	0.000	0.000	51	0.080	0.000	0.000

サンプリング：マニュアル　　屈 折 率　：1.70-0.20i
測定回数：　1　測定間隔(秒)：___　　平均回数　：　64
測定吸光度範囲 (最大値)　：0.200　(最小値)　：0.010
超音波照射時間(秒)：___　　分散時間(秒)：___

Table E: Calculation of particle size disperse factor D_4/D_1 based on Sheet D

		Volume-basis distribution (frequency)				
No	Size: D (μm)	Relative length measured by a scale	nD^3 (%)	nD	n	nD^4
1	0.099	–	0.000	0	0	0
2	0.122	–	0.000	0	0	0
3	0.15	–	0.000	0	0	0
4	0.186	–	0.000	0	0	0
5	0.229	–	0.000	0	0	0
6	0.283	–	0.000	0	0	0
7	0.35	–	0.000	0	0	0
8	0.451	–	0.000	0	0	0
9	0.533	–	0.000	0	0	0
10	0.658	–	0.000	0	0	0
11	0.812	–	0.000	0	0	0
12	1.002	–	0.000	0	0	0
13	1.237	–	0.000	0	0	0
14	1.527	–	0.000	0	0	0
15	1.885	–	0.000	0	0	0
16	2.327	–	0.000	0	0	0
17	2.873	–	0.000	0	0	0
18	3.546	–	0.020	0.001591	0.000448553	0.07092
19	4.377	–	0.270	0.014093	0.003219839	1.18179
20	5.404	–	1.060	0.036297	0.00671676	5.72824
21	6.671	–	2.410	0.054155	0.00811791	16.07711
22	8.235	–	6.710	0.098945	0.01201522	55.25685
23	10.166	–	31.870	0.308377	0.030334144	323.9904
24	12.549	–	37.870	0.240479	0.019163196	475.2306
25	15.492	–	15.660	0.065249	0.004211815	242.6047
26	19.124	–	2.250	0.006152	0.000321696	43.029
27	23.608	–	1.330	0.002386	0.000101082	31.39864
28	29.144	–	0.460	0.000542	1.85828E-05	13.40624
29	35.977	–	0.080	6.18E-05	1.71797E-06	2.87816
30	44.413	–	0.000	0	0	0
31	54.826	–	0.000	0	0	0
32	67.682	–	0.000	0	0	0
33	83.551	–	0.000	0	0	0
34	103.141	–	0.000	0	0	0
35	127.324	–	0.000	0	0	0
36	157.178	–	0.000	0	0	0
37	194.032	–	0.000	0	0	0
38	239.527	–	0.000	0	0	0
39	295.688	–	0.000	0	0	0
40	365.019	–	0.000	0	0	0
41	450.605	–	0.000	0	0	0
42	556.258	–	0.000	0	0	0
43	686.684	–	0.000	0	0	0
44	847.691	–	0.000	0	0	0
45	1046.449	–	0.000	0	0	0
46	1291.81	–	0.000	0	0	0
47	1694.701	–	0.000	0	0	0
48	1968.611	–	0.000	0	0	0
49	2430.192	–	0.000	0	0	0
50	3000	–	0.000	0	0	0
	Total→		100.000	0.828328	0.084670516	1210.853
			↑ ΣnD^3	↑ ΣnD	↑ Σn	↑ ΣnD^4

Length-average particle size $D1 = \Sigma nD / \Sigma n$	9.78
Volume-average particle size $D4 = \Sigma nD^4 / \Sigma nD^3$	12.11
Prticle size disperse factor D4/D1	**1.24**

Ref. 1

Determination of Particle Size Distributions Using Laser Diffraction

By. M. W. Wedd
maurice.wedd@malvern.co.uk

Introduction

In recent years particle sizing using the laser diffraction techniques has become the dominant method of choice. Laser diffraction units do not measure particle size distributions but carry out light scattering experiments. The relationship between the light scattered by the particles and the final particle size distribution reported depends critically upon assumptions made about the optical properties of the material under study. While the previous sentences are statements of the obvious, misleading results continue to be published due to the potential influence of time pressure, psychology and lack of formal training in optics.

Dependence of light scattering on particle size and refractive index

Light scattering occurs at refractive index gradients. If transparent glass spheres of refractive index 1.498 – 0.0 are dropped into a beaker of clean benzene (refractive index 1.498 – 0.0) they will no longer be visible. This is a condition of index matching. The higher the refractive index of the particle relative to the medium in which it is suspended, the more light will be scattered. Titanium dioxide (TiO_2) makes a strong white pigment because it has a high refractive index. The Anatase form has a refractive index of 2.54 - 0.0. Note: The first number in the refractive index number-pair 1.498 - 0.0 is the real part of the refractive index (n) and the second is the imaginary part (k), where the complex refractive index is defined as $n^* = n(1 - ik)$. If the second number is zero the material is transparent..

For homogeneous spherical particles much larger than the wavelength of the light, the scattering power varies increases in proportion to their geometric cross section or diameter squared, (D^2) the scattered light is also concentrated at low angles. For spherical particles very much smaller than the wavelength of the light the scattering power decreases in proportional to D^6 and the scattering is isotropic. When the wavelength is similar to the particle size the scattering power is a complicated function of particle size. It has a pronounced peak due to a resonant relationship between the size of the particle, its refractive index and the wavelength of the illumination (see Fig 1.) and the scattered light extends to high angles.

Fig. 1

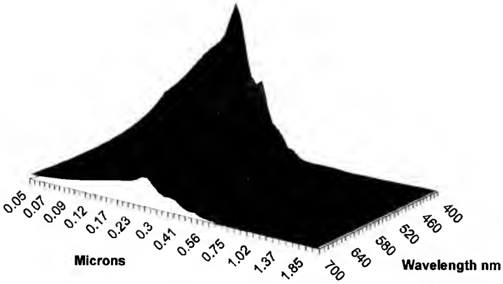


Fig. 1 -- Scattering efficiencies determined at zero angle, for equal volumes of anatase spheres RI = 2.54, plotted against particle size and wavelength in the visible wavelength region.

Pigment manufacturers try to take full advantage of the peak in the scattering power. For anatase the optimum particle size is about 0.25 microns. Figure 1 takes no account of the spectral response of the eye or of the spectral power of the illuminating source. Both of these latter points condition our appreciation of colour. Anatase pigment is nearly white because it adsorbs very little but scatters all the visible wavelengths (400 to 700 nm) nearly equally well. A yellow pigment would absorb the blue end of the visible spectrum very strongly.

With our present understanding of the physics of light scattering we can analyze the pattern of light scattered from a sphere as a function of wavelength and determine what size particle would cause this pattern.

Dependence of light scattering on the number of particles in the beam

The amount of light scattering signal recorded at the detector is a function of the scattering power of the particles. The scattering power depends on the refractive index of the solid relative to the surrounding medium. The refractive index is a complex spectral function with both real and imaginary parts. The scattering power also depends on the particle's scattering cross-section and (in the case of a distribution) the volume (or number) of particles of each size. At this point one should remember that a single 1000 µm spherical particle has the same volume as a million 10 µm spherical particles and that a single 1000 µm spherical particle has the same light-scattering power as ten thousand 10 µm particles.

At low concentrations (single scattering), doubling the concentration of particles of any one size will double the scattering contribution made by that size fraction to the total light scattering seen by the detectors. Laser diffraction instruments usually report the volume (rather than the number) of particles that have a given size because the light scattering signal is proportional to

D^2. Discriminating the tiny scattering pattern from a single small particle in the presence of the huge scattering signal from a single large particle is very difficult. If enough small particles are present to equal the volume of the single large particle the scattering of the small particles can be discriminated (separated out) and analyzed. This is why laser diffraction units usually report the volume of particles in each size class.

Dependence of light scattering on the angle of observation

Calculations using Mie theory (Ref. 1) require an input of the following parameters:
wavelength of illumination
the polarisation state of the illumination
the refractive index -- both real and imaginary -- of both the particle and the medium
the diameter of the particle
the angle of observation relative to the incident illumination (In both azimuthal planes).
The output value returned is the intensity of the scattered light from a single spherical particle viewed at the selected angle from the incident illumination. For each diameter the scattered intensity may be divided by the cube of the diameter to give the scattering intensity per unit volumes of particles for that diameter.

A particle-size instrument based on light scattering can distinguish the scattering patterns of large particles from small particles because large particles scatter strongly and principally to small angles away from the incident light beam while small particles scatter weakly and too much larger angles. Analysis of the scattering intensity as a function of observation angle can yield a particle size distribution. Rather than using a single photo-detector to scan through many angles most instrument manufacturers use an array of photo-detectors at fixed positions. It is helpful if the photo-detectors provide equal values of output current, at their angular positions for equal volumes of particles in each size class. Since a photo-detector provides an output current proportional to the intensity of the illumination multiplied by the area of the detector, laser diffraction instrument designers use small-area detectors close to the incident laser beam (low angles) and detectors with progressively larger area at larger angles of observation. The amount of light scattered into the tiny detectors (at small angles) is most influenced by the large particles, which scatter the light intensity to small angles. The amount of light scattered into the larger area detectors (at higher angles) is most influenced by the small particles, which scatter light up to the higher angles. By this means laser diffraction designers effect a balancing process which aims to provide equal information about all sizes of particles. The current output from the array of detectors at many angles is analyzed in a complex and proprietary method to arrive at a particle volume distribution.

Figure 2 illustrates the angular dependence of scattered energy using a simple weighting factor for instrument detector geometry to illustrate an ideal situation.

Fig. 2

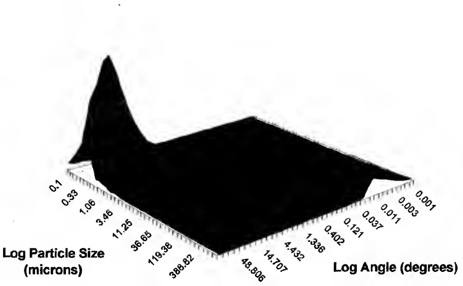


Fig 2. Light scattering energy (calculated using Mie theory) as a function of particle size and observation angle. The example is for anatase (RI = 2.54 – 0.0) in water (RI = 1.33) illuminated with He-Ne laser light (wavelength 633 nm). The particle sizes are from 0.1-microns to 1000-microns over angles ranging from 0.001-degrees to 120-degrees. The example uses equal volumes of particles for all sizes and was weighted to illustrate theoretically optimum detector geometry.

Ref. 2

Measuring particle size using modern laser diffraction techniques

Dr Paul Kippax, Product manager Diffraction Systems, Malvern Instruments Ltd
Enigma Business Park, Grovewood Road, Malvern, Worcestershire, UK, WR14 1XZ

Many different techniques have been devised for determining particle size distribution, but for a wide range of industries laser diffraction has become the preferred choice. Laser diffraction, alternatively referred to as Low Angle Laser Light Scattering (LALLS), can be used for the non-destructive analysis of wet or dry samples, with particles in the size range 0.02 to 2000 micron and has inherent advantages which make it preferable to other options for many different materials.

In this article the issues surrounding the measurement of particle size are examined. Different definitions of particle size are considered and the theory underpinning laser diffraction analysis is outlined. The benefits of laser diffraction as an analytical technique for particle sizing are discussed with reference to the Mastersizer 2000, an instrument developed by Malvern Instruments to provide easy and efficient analysis.

What is particle size?

Before discussing methods for particle sizing, it is worth understanding how particle size distributions are defined. Particles are three-dimensional objects for which three parameters (the length, breadth and height) are required in order to provide a complete description. As such, it is not possible to describe a particle using a single number that equates to the particle size. Most sizing techniques therefore assume that the material being measured is spherical, as a sphere is the only shape that can be described by a single number (its diameter). This equivalent sphere approximation is useful in that it simplifies the way particle size distributions are represented. However, it does mean that different sizing techniques can produce different results when measuring non-spherical particles.

An example of the application of the equivalent sphere approximation is shown in figure 1. Here the spherical equivalent diameters reported using different techniques for the same particle are shown. In each case, the reported diameter will be dependent on the physical property measured using the chosen technique. For example, a technique could measure the mass or volume of the particle. This would lead to the diameter of the sphere that has the same volume as the measured particle being reported as the particle size. Each representation is equally valid, although they are not equally relevant to any given process. A catalyst engineer, for example, may be particularly interested in surface area as this influences reaction rate, and might therefore prefer a technique which generates surface-area based data.

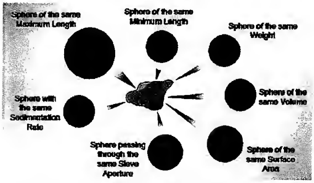

Sphere of the same Maximum Length
Sphere of the same Minimum Length
Sphere of the same Weight
Sphere of the same Volume
Sphere with the same Sedimentation Rate
Sphere passing through the same Sieve Aperture
Sphere of the same Surface Area

Fig. 1: Equivalent sphere representation for an irregularly shaped particle.

It is clear then that any instrument or technique selected for particle size analysis needs to generate data in a form that is relevant to the process. In addition, the technique needs to be reliable, simple to use and capable of generating reproducible data, if acceptance and usefulness are to be maximized.

Laser Diffraction

Laser diffraction based particle size analysis relies on the fact that particles passing through a laser beam will scatter light at an angle that is directly related to their size. As particle size decreases, the observed scattering angle increases logarithmically. Scattering intensity is also dependent on particle size, diminishing with particle volume. Large particles therefore scatter light at narrow angles with high intensity whereas small particles scatter at wider angles but with low intensity (see figure 2).

Fig. 2: Light scattering patterns observed for a large particle (upper part) and a smaller particle (lower part).

It is this behaviour that instruments based on the technique of laser diffraction exploit in order to determine particle size. A typical system consists of a laser, to provide a source of coherent, intense light of fixed wavelength; a series of detectors to measure the light pattern produced over a wide range of angles; and some kind of sample presentation system to ensure that material under test passes through the laser beam as a homogeneous stream of particles in a known, reproducible state of dispersion. The dynamic range of the measurement is directly related to the angular range of the scattering measurement, with modern instruments making measurements from around 0.02 degrees through to beyond 140 degrees (figure 3). The wavelength of light used for the measurements is also important, with smaller wavelengths (e.g. blue light sources) providing improved sensitivity to sub-micron particles.

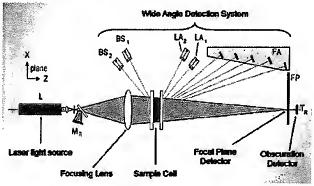


Fig. 3: Typical laser diffraction instrument layout.

Particle Size Calculations

In laser diffraction, particle size distributions are calculated by comparing a sample's scattering pattern with an appropriate optical model. Traditionally two different models are used: the Fraunhofer Approximation and Mie Theory.

The Fraunhofer approximation was used in early diffraction instruments. It assumes that the particles being measured are opaque and scatter light at narrow angles. As a result, it is only applicable to large particles and will give an incorrect assessment of the fine particle fraction.

Mie Theory provides a more rigorous solution for the calculation of particle size distributions from light scattering data. It predicts scattering intensities for all particles, small or large, transparent or opaque. Mie Theory allows for primary scattering from the surface of the particle, with the intensity predicted by the refractive index difference between the particle and the dispersion medium. It also predicts the secondary scattering caused by light refraction within the particle – this is especially important for particles below 50 microns in diameter, as stated in the international standard for laser diffraction measurements (ISO13320-1 (1999)).

Analysis of calcium carbonate

The following example illustrates the superiority of Mie Theory. Figure 4 shows comparative, cumulative particle size data for a sample of calcium carbonate, a filler used in papermaking to give a smooth printing surface.

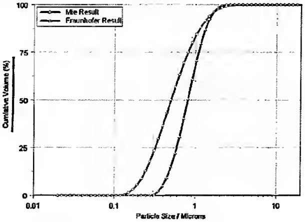


Fig. 4: Calcium carbonate size distributions reported using Mie Theory and the Fraunhofer Approximation.

Using the Fraunhofer Approximation the measured size distribution is shifted to larger particle sizes. This error stems from the inability of the Fraunhofer Approximation to correctly predict the sample's true scattering behaviour. For calcium carbonate, the scattering efficiency decreases rapidly below 2 microns, but the Fraunhofer approximation is based on the assumption that scattering efficiency is independent of particle size. The use of this approximation therefore causes a significant underestimation of the volume of sub-micron material within the sample. Mie Theory, which is able to predict effectively the fall off in scattering efficiency, gives appropriate weighting to the fine sizes and hence correctly predicts the overall particle size distribution.

The benefits of laser diffraction

Laser diffraction is a non-destructive, non-intrusive method that can be used for either dry or wet samples. As it derives particle size data using fundamental scientific principles there is no need for external calibration; well-designed instruments are easy to set up and run, and require very little maintenance. Additionally, the technique offers:

A wide dynamic measuring range – modern systems allow users to measure particles in the range from 0.02 micron to a few millimetres without changing the optical configuration, ensuring that both well-dispersed and agglomerated particles are detected equally well

Flexibility – the technique is equally applicable to sprays, dry powders, suspensions and emulsions, allowing different product formulations to be compared in a realistic way

Generation of volume-based particle size distributions – this is normally equivalent to a weight distribution and is relevant to many processes as it indicates where most of the mass of material is located in terms of particle size

Rapid data acquisition – a single measurement across the entire dynamic range can be made in 0.4 milliseconds, allowing dynamic events to be studied

High repeatability – the ability to acquire data rapidly allows many thousands of measurements to be averaged when reporting a single result, providing repeatability. This, coupled with standardized operating procedures, ensures that the instrument-to-instrument variation is less than 1%, enabling direct comparison of data from different sites.

Ease of Verification – as a first principles technique laser diffraction does not require calibration but can be easily verified using a variety of readily available NIST-traceable standards (eg from Duke Scientific, Whitehouse Scientific, NIST).

The Mastersizer 2000

The generic benefits of the technique of laser diffraction have been exploited and enhanced in the design of the Mastersizer 2000, (see figure 5), which is used worldwide for the analysis of a diverse range of particles. The Mastersizer has a fully optimized optical design which allows particles in the size range 0.02 - 2000 micron to be characterized effectively. A range of dispersion units ensures optimum sample presentation, and switching between units is relatively easy allowing different samples to be analyzed rapidly, in close succession. Automated, standard operating procedure (SOP) driven operation delivers a consistent analysis, and minimizes training requirements, whilst flexible software allows results presentation to be tailored to the requirements of the customer.

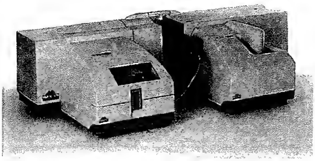


Fig. 5: Mastersizer 2000.

Application study : Powder coating characterization

One of the strengths of the laser diffraction technique is its ability to detect out-of-specification material at both the fine and coarse ends of a particle size distribution. As such, the technique is routinely applied to determine the end point of milling when producing powder coatings. Here particle size control is important as it defines the properties of the finished film as well as the ease of application. Large particles can lead to defect formation within the finished coating. However, the use of too fine a powder can lead to dusting and a reduction in the overall transfer efficiency. Achieving optimum particle size distribution in the powder coating material (often in a tightly specified range) is therefore essential to its usability and efficacy, and to the appearance and durability of the final film.

An example of the sensitivity of laser diffraction in detecting out-of-specification material is shown in figure 6. Here, the size distribution reported for a typical powder coating is shown following the addition of known fractions of coarse particles. As can be seen, the technique is extremely sensitive to the presence of the oversized material, detecting its presence at a concentration of only 2% by weight. This sensitivity derives from the intense scattering observed from coarse particles due to their large volume.

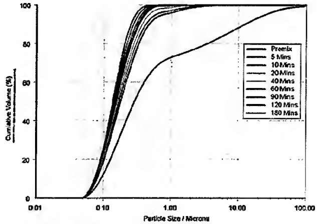


Fig. 6: Particle size distributions measured for a powder coating containing differing volumes of a coarse particle fraction.

Conclusion

Relevant, reproducible particle size data are essential in many areas of manufacturing industry and laser diffraction is a widely used technique. The Mastersizer 2000, for example, is a fully optimized laser diffraction instrument which allows manufacturers to simply and rapidly generate high quality data. These data are invaluable for quality control and in the optimization and development of materials.

i Contact / Request Information

Additional information

Malvern Instruments GmbH
Herrenberg, Germany

Malvern

Company

- Buyer's Guide entry of Malvern Instruments GmbH

News

- Malvern's webinar program doubles in size
- Malvern kicks off 2009 with new series of laser diffraction masterclasses
- Malvern Spraytec in dusty plumes!

more news

Articles

- On-line particle analysis in wet processes

- Particle shape - an important parameter in pharmaceutical manufacturing
- Making the connection - particle size, size distribution and rheology

more articles

Products

- Advanced particle characterization - robust, validated and made simpla
- Malvern Instruments presents the Zetasizer series of systems
- Malvern Kinexus 'redefines the rheometer'

more products

Top

© 2006-2010 Chemie.DE Information Service GmbH
a Life Science Network Division

www.Bionity.COM www.ChemEurope.COM www.Quimica.ES www.ChemieKarriere.NET www.BioKarriere.NET